Particle composition measurements during CLOUD7

Michael Lawler, James Smith, Paul Winkler, and CLOUD Collaboration

Citation: AIP Conference Proceedings **1527**, 385 (2013); doi: 10.1063/1.4803284

View online: http://dx.doi.org/10.1063/1.4803284

View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1527?ver=pdfcov

Published by the AIP Publishing

Particle Composition Measurements During CLOUD7

Michael Lawler[a,b] , James Smith[b,a], Paul Winkler[c], and the CLOUD collaboration

[a]*University of Eastern Finland, Kuopio, Finland*
[b]*National Center for Atmospheric Research, Boulder, USA*
[c]*Department of Physics, University of Vienna, Vienna, Austria*

Abstract. The chemical composition of >8 nm diameter aerosol was measured using the Time-of-Flight Thermal Desorption Chemical Ionization Mass Spectrometer (TOF-TDCIMS) during CLOUD7 particle nucleation experiments in Fall 2012 at the CLOUD chamber at CERN in Geneva, Switzerland. Sulfate dominated the negative ion particle spectra during all events with enough particle mass to observe, both in experiments with amine and alpha-pinene. Ammonium was also a major particle constituent during all observable events, though gaseous ammonia was present in the chamber only as a contaminant. During nucleation events following the oxidation of alpha-pinene, highly oxidized organic acids such as oxalic and oxoacetic acid were observed to be significant components of the collected aerosol.

Keywords: Nanoparticles. New particle formation, Nanoparticle growth and composition.
PACS: 92.60.Mt, 82.33.Tb.

CHEMISTRY OF PARTICLE GROWTH

Atmospheric new particle formation may play important roles in human health and climate. However, the relevant physical and chemical mechanisms for particle nucleation and growth are still incompletely understood, thus hindering related modeling efforts. One key aspect that is fundamental to developing modeling approaches that assess the global impacts of particle formation is the identification of specific chemical species or classes of compounds that contribute significantly to nanoparticle growth.

TDCIMS Instrument

The Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) addresses the need for a better understanding of atmospheric new particle formation by measuring the chemical composition of recently formed particles[1]. The TDCIMS collects ambient particles by charging and then electrostatically precipitating them onto a charged filament. Particles are charged by passing them through a pair of unipolar chargers (UPCs) which contain ^{210}Po radioactive sources. Often the particles are then size-selected by a differential mobility analyzer, but in this study all particles were collected to maximize sample. The charged nanoparticles then pass into a tube

Nucleation and Atmospheric Aerosols
AIP Conf. Proc. 1527, 385-388 (2013); doi: 10.1063/1.4803284

containing a loop of Pt wire, to which an attractive high voltage is applied while a sheath flow of clean nitrogen provides isolation from neutral aerosols and gases. Charged particles are electrostatically driven across the sheath flow to the Pt wire. The sampled size depended on the aerosol size distribution in the CLOUD chamber, which was measured with a Scanning Mobility Particle Sizer (SMPS). Collected particles were typically in the diameter range of 8-50 nm. After a collection period of typically 30 minutes, the wire is translated into a radioactive ion source region where the wire is resistively heated, causing particle constituents to desorb from the wire. Reagent ions generated by the ^{241}Am ion source, typically O_2^- and H_3O^+ and clusters of these ions with water, chemically react with the desorbed compounds for characterization by mass spectrometry. Both positive and negative ions are observed, but only one polarity is monitored at a given time. Background signal is assessed by performing the operations described above, but without a high voltage applied to the collection wire. Reported collected aerosol ion signals are corrected for this background signal and normalized by the largest reagent ion.

TDCIMS OBSERVATIONS

DMA + H_2SO_4 Nucleation

During the CLOUD7 experiments, the TDCIMS measured the composition of particles formed by nucleation involving the addition of H_2SO_4 and dimethylamine (DMA) to the chamber. The primary positive ions observed in these experiments were $(H_2O)NH_4^+$, $C_2H_8N^+$, and $C_2H_6NO^+$ (Figure 1). NH_4^+ was also observed, but the signal for $(H_2O)NH_4^+$ was larger. $C_2H_8N^+$ is protonated DMA, and $C_2H_6NO^+$ appears to be an oxidation product of dimethyl amine, n-methyl formamide. The appearance of this ion is unique to these experiments: during earlier laboratory experiments performed using amine standards we did not observe this ion[2]. We are still investigating whether this DMA oxidation product was generated in the chamber or in some stage of analysis. The main negative ion was SO_5^-, and some SO_4^- was also present. These ions are typically observed during calibration with laboratory-generated sulfate salts[3].

In experiments with 40 ppt DMA and residual NH_3 (<10 ppt) in the chamber, the NH_3 signal was comparable to that of DMA, and about half the signal of the formamide. The instrument sensitivities to DMA and NH_3 are probably not greatly different, considering their similar physical characteristics, indicating that NH_3 was probably more efficiently taken up onto the particles than was DMA. In general the spectra were very clean, similar to ammonium sulfate aerosol generated by a nebulizer, with the exception of the presence of DMA and methyl formamide. The similarity of these spectra to ammonium sulfate calibration particles suggests that the sample particles were close to pH-neutral.

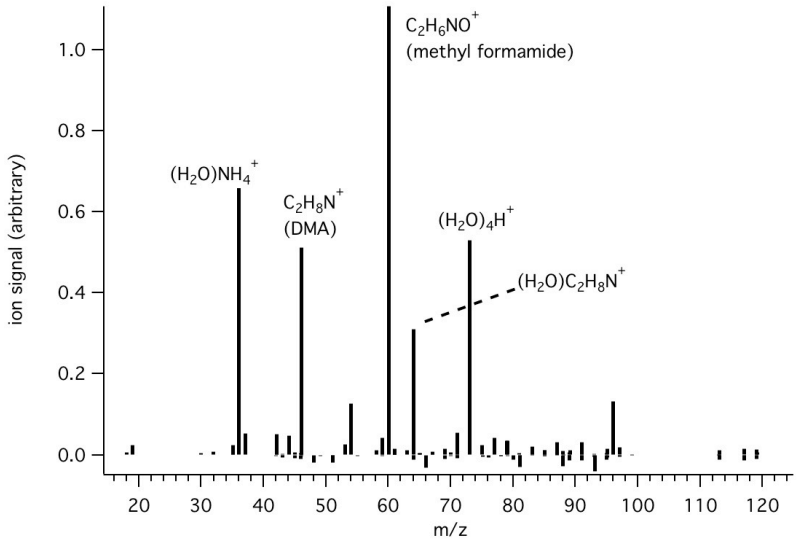

FIGURE 1. A positive ion mass spectrum for particles collected during a nucleation event with H_2SO_4, 40 ppt of gas phase DMA, and trace NH_3.

Alpha-Pinene + H_2SO_4 Nucleation

Particles formed from H_2SO_4 and the ozonolysis products of alpha-pinene were also characterized during CLOUD7. Like the DMA + H_2SO_4 spectra, these also showed high ammonia and sulfate signals, but additionally there were significant levels of organic species, both in the positive and negative spectra. The largest clearly identifiable organic peaks in the negative ion spectrum were highly oxidized organic acids such as oxalic acid and oxo-propanoic acid (Figure 2). Some non-N-containing organic species were detected at even masses, potentially indicating the presence of radical clusters. In the positive ion spectrum, acetone was identified as a major peak. This relatively volatile gas is most likely a common fragment from larger compounds, not a major nanoparticle constituent. The negative spectra also showed generally higher levels of NO_2^- than in the DMA experiments. It is not clear what the main source of NO_2^- was, but in lab tests inorganic nitrates generate this ion.

The dominant organic signals observed were at relatively low molecular masses. This may indicate that the condensing species have been significantly fragmented either during particle growth and aging or during the process of desorption and ionization. In general, some fragmentation has been observed in laboratory studies of organic acids, but typically a parent ion is also detectable. The presence of NO_2^- is puzzling since no nitrogen oxides were intentionally added to the chamber, but it may be a constant contaminant and simply reflect changes in the collected particle matrix, e.g. the particle acidity. Further laboratory tests should inform these questions.

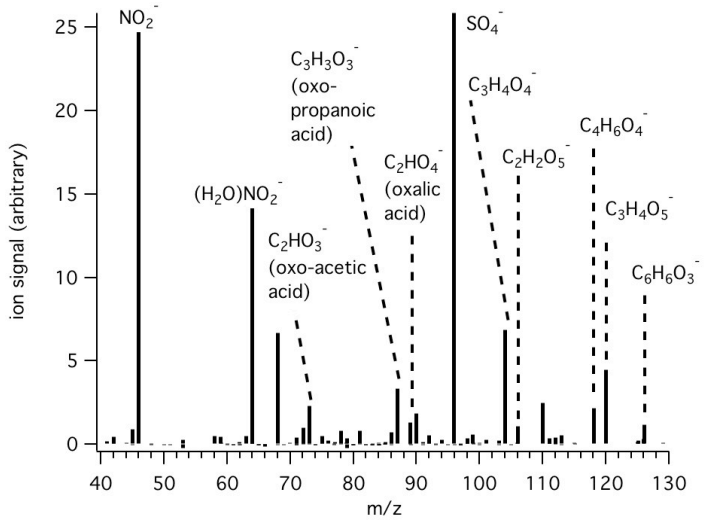

FIGURE 2. A negative ion mass spectrum for particles collected during an event involving alpha-pinene oxidation products and H_2SO_4.

ACKNOWLEDGMENTS

We would like to thank CERN for supporting CLOUD with important technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC Seventh Framework Programme (Marie Curie Initial Training Network "CLOUD-ITN" no. 215072, MC-ITN "CLOUD-TRAIN" no. 316662, and ERC-Advanced "ATMNUCLE" grant no. 227463), the German Federal Ministry of Education and Research (project nos. 01LK0902A and 01LK1222A), the Swiss National Science Foundation (project nos. 200020_135307 and 206620_130527), the Academy of Finland (Center of Excellence project no. 1118615), the Academy of Finland (135054, 133872, 251427, 139656, 139995, 137749, 141217, 141451), the Finnish Funding Agency for Technology and Innovation, the Nessling Foundation, the Austrian Science Fund (FWF; project no. P19546 and L593), the Portuguese Foundation for Science and Technology (project no. CERN/FP/116387/2010), the Swedish Research Council, Vetenskapsrådet (grant 2011-5120), the Presidium of the Russian Academy of Sciences and Russian Foundation for Basic Research (grants 08-02-91006-CERN and 12-02-91522-CERN), and the U.S. National Science Foundation (grants AGS1136479 and CHE1012293).

REFERENCES

1. Smith, J. N., K. F. Moore, P. H. McMurry, and F. L. Eisele (2004), Atmospheric measurements of sub-20 nm diameter particle chemical composition by thermal desorption chemical ionization mass spectrometry, *Aerosol Science and Technology*, *38*(2), 100-110.
2. Smith, J. N., K. C. Barsanti, H. R. Friedli, M. Ehn, M. Kulmala, D. R. Collins, J. H. Scheckman, B. J. Williams, and P. H. McMurry (2010), Observations of aminium salts in atmospheric nanoparticles and possible climatic implications, *Proceedings of the National Academy of Sciences*.
3. Voisin, D., J. N. Smith, H. Sakurai, P. H. McMurry, and F. L. Eisele (2003), Thermal desorption chemical ionization mass spectrometer for ultrafine particle chemical composition, *Aerosol Science and Technology*, *37*, 471 - 475.